

Express Mail Label No.: ET844496320USDate of Deposit: February 27, 2002

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ABRASION- AND WRINKLE-RESISTANT FINISH FOR TEXTILES

10 The present invention is a continuation application of co-pending International Patent Appln. No. PCT/US00/24581, filed September 8, 2000 and designating the United States of America, which application claims the benefit of Provisional U.S. application Ser. No. 60/153,375, filed September 10, 1999; the entire disclosures of which are incorporated herein by reference.

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FIELD OF THE INVENTION

The present invention relates to textile treatment compositions for imparting permanent abrasion- and wrinkle-resistance to textiles.

BACKGROUND OF THE INVENTION

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Cotton consists of cellulose, a polysaccharide. The cellulose molecules in a cotton fiber are arranged linearly and pass in and out of crystalline and amorphous regions and are held in place by hydrogen bonds between the molecules. Slippage between the cellulose chains or between larger structural units of the fiber occurs when a force of sufficient magnitude is placed on the fiber. The hydrogen bonds tend to resist or prevent the slippage, but once slippage occurs the bonds reform in new locations and tend to maintain the fiber in the bent or wrinkled state. In addition, cotton fiber is hydrophilic and absorbs water, which can break hydrogen bonds and allow the fiber or fabric to shrink. Thus, 100% cotton wrinkles easily and has the potential to shrink upon laundering.

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30 Cellulose is made up of repeating anhydroglucose units. Each unit contains two secondary and one primary alcohol groups. To achieve wrinkle resistance, alcohol groups on adjacent cellulose chains are partially crosslinked to keep the chains fixed relative to each other. Over the years, a number of crosslinking agents (resins) have

been explored to achieve durable-press properties. Some include isocyanates, epoxides, divinylsulfones, aldehydes, chlorohydrins, N-methylol compounds, and polycarboxylic acids. Of these, N-methylol compounds have been used the most. Examples include dimethylol urea, dimethylol ethylene urea, trimethylol trazine, dimethylol methyl carbamate, uron, triazone, and dimethylol dihydroxy ethylene urea. Dimethylol dihydroxy ethylene urea (DMDHEU) is the most common durable-press finish used today.

Resins improve wrinkle recovery, fabric smoothness, dimensional stability, washfastness of some dyes, pilling resistance, ease of ironing, durability of finishes (repellents, hand modifiers, embossing, etc.), and general appearance. However, crosslinking has its disadvantages, including loss in tear and tensile strength, loss in abrasion resistance, reduced moisture regain, possible damage due to chlorine retention, potential odors, potential discoloration, and sewing problems. Durable-press fabrics also often have stiff, harsh, uncomfortable fabric tactile (hand) properties. Therefore, fabric softeners/lubricants are commonly added to these fabrics to mitigate some of these deficiencies. Softeners improve the hand of the fabric as well as increase abrasion resistance and tear strength. The softener also functions as a sewing lubricant. There are four basic types of softeners – anionic, cationic, nonionic, and blended systems.

The anionic softeners are generally sulfated or sulfonated compounds used primarily to lubricate yarns through processing. Examples of these compounds include sulfonated tallow, glycerides, and esters. Sulfonated or sulfated castor oil, propyl oleate, butyl oleate, and tallow are used in various steps in dyeing fabrics. Anionics tend to provide inferior softness compared to the cationics and nonionics. Furthermore, they have limited durability to laundering or dry-cleaning. Their major limitation comes from their negative charge, which causes incompatibility in resin finishing baths and makes them most sensitive to water hardness and electrolytes.

The cationic softeners are nitrogen-containing compounds including fatty amino amides, imidazolines, amino polysiloxanes, and quaternaries. As a result of their positive charge, they are attracted to cotton or synthetic fabrics through electrostatic interactions. They tend to be compatible with most resin finishes and are somewhat

durable to laundering. The most significant disadvantage of cationic softeners is their tendency to change the shade or affect the fastness of certain dyestuffs. Discoloration on white fabrics may also be a concern. The development of a fishy odor on the fabric can be a problem with certain systems.

5 Nonionics are the most widely used softeners. This class includes polyethylenes, glycerides such as glycerol monostearate, ethoxylates such as ethoxylated castor wax, coconut oil, corn oil, etc., and ethoxylated fatty alcohol and acids. The nonionic softeners offer excellent compatibility in resin baths due to their uncharged state. Since nonionics have no charge, they have no specific affinity for
10 fabrics and therefore have relatively low durability to washing.

To optimize softening and lubricating properties, many manufacturers tend to formulate a softener containing both nonionic and cationic types. Typically, an aminosilicone or an imidazoline for a silky soft slick hand will be blended with a cationic or a nonionic polyethylene lubricant for sewability and tear- and abrasion-strength
15 properties. Increased customer demand for improved durability and useful life of a garment has led to the use of high-density polyethylenes as softeners. Polyethylenes have decreased solubility in detergent solutions, which results in increased softener durability. However, the disadvantages of the softeners (such as, for example, lack of durability to repeated launderings) remain.

20 SUMMARY OF THE INVENTION

This invention is directed to treatment preparations useful for the permanent or substantially permanent treatment of textiles and other webs to provide tear and abrasion strength and softness to durable-press garments. The preparations comprise
25 a softener (referred to herein as a "resin-reactive modifier") durable to repeated laundering used in conjunction with a durable-press resin, to increase the comfort and lifetime of durable-press garments. More particularly, the preparations of the invention comprise a "rubbery" resin-reactive modifier capable of reacting with a durable-press resin during textile treatment. By "reacting" is meant that the polymer will form a
30 covalent bond with the durable-press resin and the resin will form a covalent bond to the fiber, textile, or web to be treated. The resulting durable-press/softener preparation is

substantially permanently attached to the web and provides improved softness and tear/abrasion strength retention within and/or on the textile or web fiber structure while retaining the durable-press properties of the resin through repeated launderings.

5 This invention is further directed to the yarns, fibers, fabrics, textiles, finished goods, or nonwovens (encompassed herein under the terms "textiles" and "webs") treated with the textile-reactive durable-press/softener preparation. Such textiles and webs exhibit a greatly improved, durable softness and tear/abrasion strength. By "durable softness and tear/abrasion strength" and "durable wrinkle resistance, a soft hand, and tear/abrasion resistance" are meant that the textile or web will exhibit
10 improved softness and resistance to tear and/or abrasion, even after multiple launderings, while retaining its durable press or resistance to wrinkling.

Methods are provided for treating fabrics to impart permanent wrinkle resistance as well as permanent softness and tear/abrasion resistance by combining a "rubbery" resin-reactive modifier with durable-press resins.

15 DETAILED DESCRIPTION OF THE INVENTION

The textile-reactive preparations of the invention comprise a combination of i) a durable-press resin capable of imparting wrinkle resistance and ii) a resin-reactive modifier capable of imparting a soft hand and tear/abrasion resistance to textiles.

20 The resin-reactive modifier useful in the present invention comprises particular monomers, oligomers, or polymers having hydroxyl- or other reactive group-containing monomers, or mixtures thereof (referred to herein and in the appended claims as "reactive building blocks"), copolymerized with soft, rubbery or elastomeric monomers or polymers (referred to herein and in the appended claims as "rubbery building
25 blocks"). The resin-reactive modifier may also comprise rubbery building blocks that are processed post-polymerization to include hydroxyl- or other reactive groups. The resin-reactive modifier is capable of reacting with a durable-press resin during textile treatment. By "reacting" is meant that the resin-reactive polymer will form a covalent bond with the durable-press resin. The resin in turn will form a covalent bond to the
30 fiber, textile, or web to be treated. The resin-reactive modifier will impart a soft hand to the resin-treated textile and also provide tear and/or abrasion resistance to the textile.

This resin-reactive modifier, because of its covalent bonding to the textile through the wrinkle-resistant resin, is durable to laundering and is permanent, and it significantly increases the comfort and lifetime of durable-press garments.

The rubbery groups of the resin-reactive modifier are selected from those groups that will provide the necessary softness and tear/abrasion resistance. Examples include polymers of isoprene, chloroprene, butadiene, ethylene, isopropylene, ethyleneoxide, isobutylene, propylene, chlorinated ethylene, and polymers such as polydimethylsiloxane, polyisobutylene, poly-alt-styrene-co-butadiene, poly-random-styrene-co-butadiene, etc., and copolymers of all of these. The rubbery group is copolymerized in such a proportion as to take about 60% to about 99.8% by weight, preferably about 80% to about 95% by weight, of the resin-reactive modifier copolymer of this invention.

The reactive groups on the resin-reactive modifier are selected from those groups that will bind chemically with a particular durable-press resin. For example, groups may consist of hydroxyls, amines, amides, or thiols. In a presently preferred embodiment, the resin modifier is selected from polymers containing at least one hydroxyl group per molecule.

The durable-press resin is chosen from those that will bind chemically with a particular fiber, yarn, fabric, or finished good. For example, cellulosic-based webs such as paper, cotton, rayon, linen, and jute contain hydroxyls. Wool, which is a proteinaceous animal fiber, contains hydroxyls, amines, carboxylates, and thiols.

Specific amine-reactive groups (for reaction with wool, for example) include isothiocyanates, isocyanates, acyl azides, N-hydroxysuccinimide esters, sulfonyl chlorides, aldehydes and glyoxals, epoxides and oxiranes, carbonates, arylating agents, imidoesters, carbodiimides, anhydrides (such as maleic anhydride), and halohydrins. Carboxylate-reactive groups (for reaction with wool, e.g.) include diazoalkanes and diazoacetyl compounds, carbonyl diimidazole, and carbodiimides. Hydroxyl-reactive chemical reactions (for, e.g., wool and cotton) include couplings with epoxides and oxiranes, carbonyl diimidazole, N,N'-disuccinimidyl carbonate or N-hydroxysuccinimidyl chloroformate, alkyl halogens, isocyanates, and halohydrins, oxidation with periodate, and enzymatic oxidation. Examples of thiol-reactive chemical reactions (for wool, for

example) include couplings with haloacetyl and alkyl halide derivatives, maleimides, aziridines, acryloyl derivatives, arylating agents, and disulfide-forming reactions mediated by exchange reagents (such as pyridyl disulfides, disulfide reductants, and 5-thio-2-nitrobenzoic acid, for example).

5 Durable-press resins useful in the present invention include isocyanates, epoxides, divinylsulfones, aldehydes, chlorohydrins, N-methylol compounds, and polycarboxylic acids, which compounds are known to those of skill in the art. N-methylol compounds have been used the most. Examples include dimethylol urea, dimethylol ethylene urea, trimethylol trazine, dimethylol methyl carbamate, uron, 10 triazone, and dimethylol dihydroxy ethylene urea (DMDHEU. Additionally, in the case of cotton, any compound capable of forming a crosslink between two hydroxyl groups may be used as the resin component.

15 In a presently preferred embodiment, the durable-press/softener preparation comprises i) a resin modifier selected from polymers consisting of butadiene or hydrogenated butadiene containing at least one hydroxyl group per molecule, and ii) the resin DMDHEU or cyanuric chloride.

20 In forming the durably soft, tear/abrasion-resistant textile, additional crosslinkers or complementary reactive functionalities may also be added to the solution of the durable-press/softener preparation to help create bridges between crosslinkable groups, to alter the crosslink density, and/or to add additional properties to the textile (for example water and stain resistance).

25 The present invention is further directed to the yarns, fibers, fabrics, textiles, or finished goods (encompassed herein under the terms "textiles" and "webs") treated with the durable-press/softener preparation. These novel textiles or webs will display comparable durable-press performance without the harsh hand or the low tear and low abrasion resistance of traditional durable-press textiles.

30 These textiles, which exhibit wrinkle resistance, a soft hand, and improved tear/abrasion resistance, can be used in a variety of ways including, but not limited to: clothing, especially those for, but not limited to easily wrinkled clothing, such as formal garments, coats, hats, shirts, pants, gloves, and the like; other textiles subject to wear or tearing, such as awnings, draperies, upholstery for outdoor furniture, protective

covers for barbecues and outdoor furniture, automotive upholstery, sails for boats, and the like; and industrial uses, such as those listed in Adanur, S., *Wellington Sears Handbook of Industrial Textiles*, p. 8-11 (Technomic Publishing Co., Lancaster, PA, 1995).

5 The novel webs of the present invention are intended to include fabrics and textiles, and may be a sheet-like structure (woven, knitted, tufted, stitch-bonded, or non-woven) comprised of fibers or structural elements. The fibers may include non-fibrous elements, such as particulate fillers, binders, sizes and the like. The textiles or webs include fibers, woven and non-woven fabrics derived from natural or synthetic fibers or
10 blends of such fibers, as well as cellulose-based papers, and the like. They can comprise fibers in the form of continuous or discontinuous monofilaments, multifilaments, staple fibers, and yarns containing such filaments and/or fibers, which fibers can be of any desired composition. The fibers can be of natural, man-made, or synthetic origin. Mixtures of natural fibers, man-made fibers, and/or synthetic fibers can also be used. Examples of natural fibers include cotton, wool, silk, jute, linen, and the like. Examples of man-made fibers include regenerated cellulose rayon, cellulose acetate and regenerated proteins. Examples of synthetic fibers include polyesters (including polyethyleneglycolterephthalate), polyamides (including nylon), acrylics, olefins, aramids, azlons, modacrylics, novoloids, nitrils, aramids, spandex, vinyl
15 polymers and copolymers, vinal, vinyon, and the like.

20 To prepare the permanent durable-press, soft, and tear/abrasion-resistant webs, the fiber, the yarn, the fabric, or the finished good (the "textile" or "web") is exposed to the resin-reactive modifier suspended in an aqueous solution in the presence of a suitable durable-press resin and suitable catalyst for activating the resin (such as, for
25 example, $MgCl_2$ or any Lewis acid), by methods known in the art such as by soaking, spraying, dipping, fluid-flow, padding, and the like. The resin-reactive modifier and the durable-press resin may be added together to the solution with the web or they may be added sequentially. The textile-reactive functional groups of the durable-press resin react with the web, by covalent bonding, to permanently attach to the web. The resin-
30 reactive functional groups on the permanent softener-tear/abrasion resistant polymer react with the durable-press resin, by covalent bonding. The durable-press resin serves

to crosslink the cellulose chains, in the case of cotton for example, while at the same time reacting with the reactive group-containing resin-reactive modifier, thus serving as a covalent bridge between the cellulose and the resin-reactive modifier. The modifier may be linked by one or multiple hydroxyls to the cellulose through the resin. The treated web is then removed from the solution, dried, and cured.

The concentration of the resin-reactive modifier in solution can be from about 0.1 wt% to about 10 wt%, preferably from about 2 wt% to about 8 wt%, more preferably about 8 wt%; depending, however, on the characteristics of the particular resin-reactive modifier selected (such as molecular weight or material) and on the amount of softening and tear/abrasion resistance desired.

The concentration of the durable press resin may vary, depending on the particular resin used and the final characteristics of the product desired. For example, in the case of DMDHEU, the manufacturer of the resin recommends 8 wt% DMDHEU to obtain permanently pressed textiles, whereas a lower amount may be used when abrasion resistance without permanent press is desired.

The process temperature can vary widely, depending on the affinity of the durable press resin for the web substrate and for the resin-reactive modifier. However, the temperature should not be so high as to decompose the reactants or so low as to cause inhibition of the reaction or freezing of the solvent. Unless specified to the contrary, the processes described herein take place at atmospheric pressure over a temperature range from about 120°C to about 180°C, more preferably from about 140°C to about 160°C, and most preferably at about 150°C. The time required for the processes herein will depend to a large extent on the temperature being used and the relative reactivities of the starting materials. Therefore, the time of exposure of the textile to the polymer in solution can vary greatly, for example from about one minute to about two hours. Normally, the exposure time will be from about one to about five minutes. Following exposure, the treated yarn or fabric is dried at ambient temperature or at a temperature above ambient, up to about 90°C, possibly higher. The pH of the solution will be dependent on the requirements of the resin, the resin-reactive modifier, and the textile. Typically, resin-crosslinking is optimized at low pH, but cotton, for example, degrades in acid, so a balance must be reached. Furthermore, the deposition

of resin-reactive modifiers with charged groups (e.g., amines, carboxylates, and the like) is expected to be dependent on solution pH. Salts (such as, for example, NaCl) may optionally be added to increase the rate of adsorption of anionic and cationic polymers onto the fibers. Unless otherwise specified, the process times and conditions are intended to be approximate.

EXAMPLES

Example 1: Preparation of Resin-Reactive Modifier Solution

Four percent (4%) by weight of hydroxy-terminated polybutadiene (PBD-OH, 1200MW, [hydroxyl] = 1.7 meq/g, CAS# 69102-90-5, Aldrich, Milwaukee, WI) and 4% by weight of Tween-40 (polyoxyethylene sorbitan ester, ICI Surfactants, Wilmington, DE) were added to water with stirring to give an aqueous solution of hydroxy-terminated resin-reactive modifier.

Example 2: Application of Durable-Press/Softener Preparation to 100% Cotton, and Physical Characterization

Cotton fabric samples (400 series, Test Fabrics, West Pittston, PA) were treated in stirred aqueous solutions containing various percentages of hydroxy-terminated polybutadiene and Tween-40, prepared as described in Example 1 above. The samples were removed and dried at 85°C for 10 minutes. The samples were then treated with a commercial preparation of durable press resin (Freerez 901, 38% buffered DMDHEU, BF Goodrich, Greenville, SC) and catalyst (Freecat LF, MgCl₂ and citric acid, BF Goodrich, Greenville, SC) according to the manufacturer's specifications at 8% and 2% on bath weight, respectively. Fabric samples were dipped in 200% of fabric weight resin and catalyst solution and padded to 100% pick-up. Samples were dried at 85°C for 10 minutes, followed by curing at 160°C for 4 min. Samples were tested for flex abrasion (measured using an ASTM 03885-92, at 4 lb tension and 1 lb pressure) and wrinkle recovery (following the AATCC test method #66-1998).

Additionally, samples were washed in an accelerated laundering machine to simulate five home launderings. All sample treatments were done to mimic a dip, pad, squeeze application method with approximately 100% wet pick-up. The results are shown in Table I.

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Table I. Wrinkle recovery angle and flex abrasion cycles of various samples.

Sample	% PBD-OH	% DMDHEU	# Home Launderings	Wrinkle Recovery Angle	Flex Abrasion Cycles
Pure Cotton 0 HL	0	0	0	72°	329 ± 129
Pure Cotton 5 HL	0	0	5	70°	455 ± 95
DMDHEU Treated Cotton – 0 HL	0	8	0	135°	168 ± 91
DMDHEU Treated Cotton- 5 HL	0	8	5	120°	138 ± 100
PBD-OH/DMDHEU Treated Cotton – 0 HL	4	8	0	128°	585 ± 120
PBD-OH/DMDHEU Treated Cotton – 5 HL	4	8	5	127°	737 ± 291